

Proximity coupling of granular film with ferroelectric substrate and giant electro-resistance effect

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(Dated: May 22, 2015)

We study electron transport in granular film placed above the ferroelectric substrate. We show that the conductivity of granular film strongly depends on the ferroelectric state due to screening effects which modify the Coulomb blockade in granular film. In particular, the electric current in granular film is controlled by the direction of ferroelectric polarization. We show that the ferroelectric/granular film system has a large electro-resistance effect. This effect can be utilized in memory and electric field sensor applications.

PACS numbers: 77.80.-e, 73.23.Hk, 85.50.Gk, 72.80.Ng

I. INTRODUCTION

Ferroelectric materials were known for a long time, nearly a century. Currently ferroelectric materials attract a lot of attention for two reasons: on one hand, due to the availability of new kind of ferroelectrics (FE) for experiment including ultrathin films, lateral confined and hybrid ferroelectric nanoparticles, and granular ferroelectrics;¹⁻⁵ on the other hand, due to the promising potential applications of new ferroelectric materials. New physics emerges in these materials compared to the bulk ferroelectric materials investigated in the past. Electric properties of ultrathin films are qualitatively different from their bulk counterparts.^{3,6} New phases such as electric vortices appear in ferroelectric nanoparticles.¹ Combination of ferroelectric films with ferromagnetic layers produces a strong strain and charge mediated magneto-electric coupling.^{7,8} All these discoveries are giving a new lease of life to this field.

The fundamental question in this field is the influence of the FE polarization on transport properties. This issue is crucial for memory applications since the direction of the FE polarization can be used for data coding. In this case the mechanism of data writing involves the electric field rather than the electric current. This is the advantage of the FE based memory allowing to essentially reduce the energy consumption.

There are several ways to determine the direction of the FE polarization: 1) the tunneling electro-resistance effect in FE tunnel junctions with tunneling current being dependent on the direction of the FE polarization.⁹⁻¹¹ This method requires very thin FE barriers, thus reducing the FE Curie temperature and the electric polarization of the FE barrier. 2) The rectification effect in the Schottky diode at the ferroelectric/metal interface.¹²⁻¹⁵ This effect changes the sign by switching the FE polarization. 3) The transistor type structures with FE being placed in between the gate electrode and the transistor channel. This method uses electric charges on the surface of

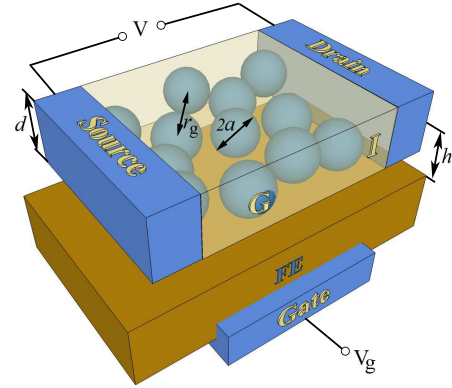


FIG. 1. (Color online) Sketch of ferroelectric/granular film system with granular film of thickness d being placed at distance h above the ferroelectric (FE) layer. Granular film consists of metallic grains (G) with average size $2a$ and intergrain distance r_g embedded into an insulating matrix (I). V and V_g are the bias and the gate voltages, respectively.

the FE to control the current in the channel.¹⁶⁻¹⁸ Unfortunately the complexity of "good" FE/semiconductor surfaces does not allow the realization of this type of memory now.¹⁸

In this paper we introduce a new mechanism for finding the direction of the FE polarization using the granular thin film, with metallic grains embedded in an insulating matrix, for transistor channel, Fig. 1. We assume that grains have nanometer range sizes with well developed Coulomb blockade in granular film. The main parameter characterizing the Coulomb blockade in granular materials is the charging energy which is the electrostatic energy of a single excess electron placed on a single grain. Charging the charging energy one can control the electron transport in granular systems.

Recently it was shown that the FE matrix influences the charging energy in granular ferroelectrics – materials consisting of metallic grains embedded into a FE ma-

trix.¹⁹ In this paper we propose an essentially different geometry: the FE film being placed between the gate electrode and the channel/granular film, Fig. 1. Since the Coulomb interaction is the long range interaction the presence of the FE layer will influence the charging energy in granular film and will define the electron transport in granular channel. In contrast to the field effect transistor (FET) with semiconducting channel, where the FE polarization changes the position of the chemical potential in the channel leaving the band gap unchanged, in the FET with granular channel the ferroelectric dielectric permittivity influences the width of the "forbidden band" (determined by the charging energy).

The chosen geometry in Fig. 1 allows: 1) to control the FE state using the gate voltage without inducing the electric current in the system; 2) to identify the FE state using the current along the granular film without affecting the FE substrate; and 3) to avoid surface problems existing in the case of semiconductor/FE transistor.

In this paper we show that: 1) the source to drain current in the system in Fig. 1 depends on the direction of the FE polarization and the gate voltage and 2) the temperature and electric field dependence of dielectric permittivity can be studied using the conductivity of granular film.

The paper is organized as follows: In Sec. II A-II C we introduce the model and discuss the influence of dielectric substrate on the Coulomb energy of granular film. We study transport properties of composite system in Fig. 1 in Sec. II D-II F and discuss the validity of our model and some possible applications in the Discussion section.

II. INFLUENCE OF FERROELECTRICITY ON TRANSPORT PROPERTIES OF GRANULAR FILM

A. The system

We consider the following system: the quasi two dimensional granular film of thickness d placed above the FE substrate at distance h ($d < h$, h is the distance between the grain centres and the FE surface), Fig. 1. The film consists of metallic grains with average radius a embedded in an insulating matrix ($d \approx 2a$). The average intergrain distance is r_g . The film is confined with two leads - source and drain. A small voltage bias V is applied to the leads leading to the electric current j . There is an insulating layer with dielectric constant ϵ_1 located in between the granular film and the FE substrate. The FE substrate has the thickness $L \gg h$. The ferroelectric state is controlled by the gate electrode with voltage V_g placed beneath the FE substrate. This gate creates an external electric field E_{ext} inside the FE layer perpendicular to the film and the substrate. This external field E_{ext} does not create the electric current.

B. Ground state

For zero bias voltage the electric current is absent in the system. The FE substrate is affected by the electric field created by the gate electrode, grains, and charges existing on the FE surfaces. We assume that the granular film has small but finite conductivity. Therefore the electric field created by the surface charges of the FE is screened by the grains charges. Also we assume that the measurement time is much larger than any relaxation times in the system. Thus, all grains have the same electric potential and the field inside the FE is screened due to presence of grains²⁰. For distances $L\epsilon_1 \gg (h - a)r_g^2\epsilon^{\text{FE}}/(ha)$ the screening charge at a grain at zero gate voltage is $q^g = -Pr_g^2$ with P being the magnitude of electric polarization, Appendix A. $\epsilon^{\text{FE}} = (\epsilon_{\perp}^{\text{FE}}\epsilon_{\parallel}^{\text{FE}})^{1/2}$ is the effective dielectric permittivity of the FE substrate with $\epsilon_{\perp, \parallel}^{\text{FE}}$ being the dielectric permittivity tensor components perpendicular and parallel to the FE surface.²¹ It depends on the electric field E_{ext} applied to the FE. Corrections to the charge q^g are of the order of $(h - a)r_g^2\epsilon^{\text{FE}}/(L\epsilon_1ha)$. In this limit the external field can be written in the form, $E_{\text{ext}} = V_g/L$.

At finite gate voltage with similar accuracy we find $q^g = (-P + V_g\epsilon^{\text{FE}}/(4\pi L))r_g^2$.

We notice that the charge q^g is the average grain charge. In real systems due to electron charge quantization q^g can have integer values only for each individual grain. This leads to an additional source of disorder in the system. The polarization of typical FE's gives $q^g \gg 1e$ for grain sizes of 5 nm. Therefore we neglect this charge quantization here.

C. Transport model

The FET with semiconductor channel and with the FE in between the gate and the channel is well studied.^{16-18,22,23} In this device the FE layer controls the electron density in the channel. Screening of the FE polarization by the charges accumulated in the channel leads either to enrichment or depletion of the channel and correspondingly either to increasing or decreasing of the current in the channel.

In the current consideration the granular film plays the role of the channel. Screening of the FE polarization leads to charging of metallic grains inside the channel. Since metallic grains have large number of electrons an addition of several electrons does not influence the electron transport in contrast to the semiconductor case.²⁰

The most important parameter characterizing the properties of granular film is the charging energy E_c ,^{24,25}. In granular metals it plays a similar role as the forbidden band in semiconductors. For charging energy $E_c \gg T$ electrons are localized inside grains. The Coulomb energy in granular materials depends on the state of the FE due to screening effects.^{19,26,27} The perpendicular com-

ponent of the dielectric permittivity ϵ^{FE} of the FE can be changed using the external electric field and temperature leading to the controllable charging energy. For example, the Coulomb energy of granular metal placed above the FE substrate has the form, Appendix B²⁶

$$E_c = E_c^0 \frac{1}{\epsilon} \left(1 + \frac{a}{2h} \frac{\epsilon - \epsilon^{\text{FE}}}{\epsilon + \epsilon^{\text{FE}}} \right), \quad (1)$$

where $E_c^0 = e^2/2a$ is the Coulomb energy of the charged sphere in vacuum and ϵ is the effective dielectric permittivity of the half space above the FE substrate. The estimates of ϵ is given in Appendix B. In our consideration ϵ does not depend on the external electric field. It was shown in Ref. 26 that the FE layer is strongly influence the magnetic state of the proximity coupled granular film with magnetic grains through screening effects. Here we uncover the new physics related to the electron transport in the proximity coupled granular nonmagnetic film and the FE layer shown in Fig. 1.

To summarize, in contrast to the FET with semiconducting channel, where screening of the FE polarization changes the chemical potential in the channel leaving the band gap unchanged, in granular metals the changing of the FE dielectric permittivity modifies the forbidden band width in the channel.

1. Variable range hopping

There are several transport regimes in composite materials depending on the coupling between the grains. At weak coupling and low temperatures the electron transport is due to variable range hopping. This mechanism involves electrons with energies inside the Coulomb gap leading to the following conductivity^{28–30}

$$\sigma = \sigma_0 \exp(-(T_0/T)^{1/2}). \quad (2)$$

Here σ_0 is the high temperature conductivity proportional to the intergrain conductance. In our consideration the system is two dimensional since the film thickness is comparable with a single grain diameter and the hopping distance at low temperatures is larger than the grain size. T_0 is the characteristic temperature scale

$$T_0 = e^2/(\epsilon\xi), \quad (3)$$

where ξ is the electron localization length²⁵

$$\xi = a/\ln(E_c^2/T^2 g_t^0). \quad (4)$$

g_t^0 is the intergrain tunneling conductance.

2. Sequential tunneling

Increasing the temperature the hopping distance decreases reaching the grain size. At these temperatures

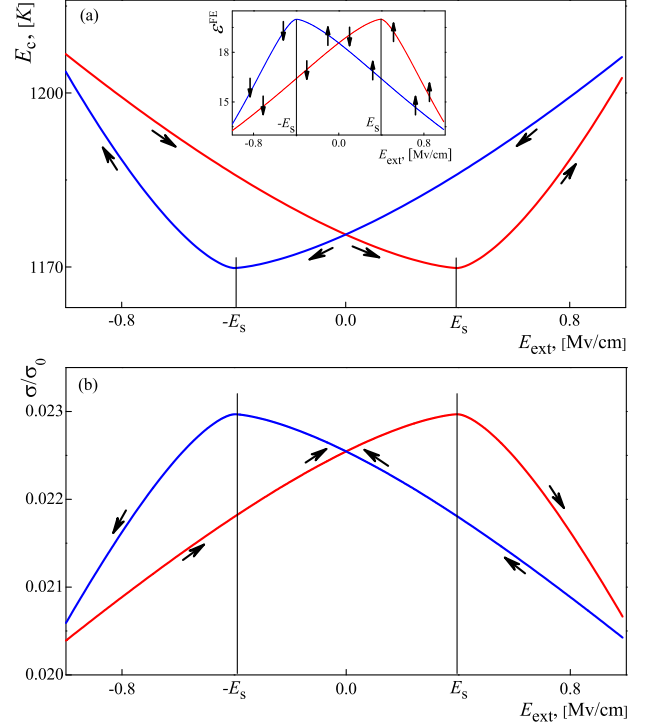


FIG. 2. (Color online) (a) Charging energy E_c in Eq. (1) vs external electric field E_{ext} for ferroelectric/granular film system shown in Fig. 1. E_s is the ferroelectric switching field. Arrows indicate the path around the hysteresis loop. Insert: dielectric permittivity vs field E_{ext} for temperatures $T < T_c^{\text{FE}}$. Vertical arrows indicate the direction of polarization of the substrate. (b) Normalized conductivity of granular film vs external field E_{ext} . Arrows indicate the path around the hysteresis loop. The following set of parameters were used: the average grain size $a = 3$ nm, the intergrain distance $r_g = 7$ nm, the dielectric permittivity of insulating matrix $\epsilon_m = 1$, the effective dielectric permittivity of the half-space above the substrate $\epsilon = 1.3$, the distance between the film and the substrate $h = 4$ nm.

and small bias voltage the conductivity has an activation behavior in the Coulomb blockade regime²⁵

$$\sigma = \sigma_0 e^{-\frac{E_c}{T}}, \quad (5)$$

with σ_0 being the high temperature conductivity proportional to the intergrain conductance.

Using Eqs. (2) and (5) we find that for temperatures $T > T_{\text{cr}} = E_c^2/T_0$ the activation transport is more important. Neglecting the logarithmic dependence of the localization length ξ on temperature for the following set of parameters $E_c \sim 10^3$ K, $g_t^0 = 0.1$, $E_c^0 \sim 1.7 \cdot 10^3$ K we find $T_{\text{cr}} \approx 100$ K. Therefore at room temperature, $T > T_{\text{cr}}$ the sequential tunneling is the main transport mechanism. For FE with room temperature transition, the transport is described by Eq. 5. For FE with Curie temperature less than T_{cr} one has to use Eq. 2.

Below we mostly discuss the high temperature limit since the FE Curie temperature is rather high. However,

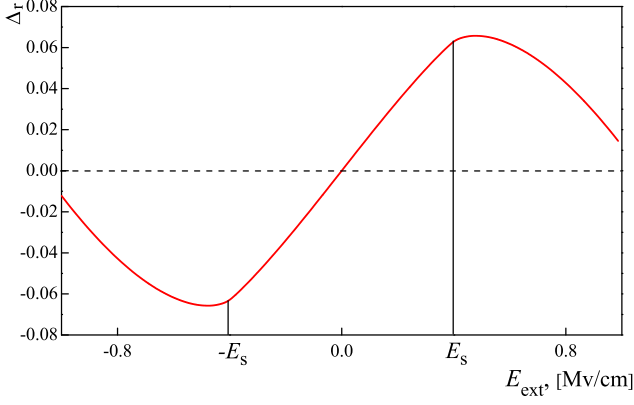


FIG. 3. (Color online) Dimensionless conductivity difference Δ_r in Eq. (6) of granular film placed above the FE substrate vs external electric field. E_s is the FE switching field.

we also provide the necessary formulas for low temperatures.

The Coulomb energy E_c in Eq. (5) depends on the dielectric permittivity ϵ^{FE} of the FE substrate which in its turn depends on the external electric field E_{ext} and temperature. Thus, applying the gate voltage V_g and therefore the external field E_{ext} we can control the conductivity of granular film. Next, we discuss two conductivity regimes — below and above the ferroelectric Curie temperature T_C^{FE} .

D. Conductivity below the Curie point

Here we discuss the conductivity of granular film for temperatures $T < T_C^{\text{FE}}$ with the FE substrate being in the FE state. In this case the polarization and the dielectric permittivity ϵ^{FE} of the FE layer have hysteresis behavior as a function of external field E_{ext} meaning that there are two different resistive states for each field depending on the hysteresis branch.

The Coulomb energy E_c in Eq. (1) depends on the dielectric permittivity ϵ^{FE} and therefore shows the hysteresis behavior, Fig. 2(a). It has a minimum for external fields close to the switching field E_s . The behavior of dielectric permittivity vs external field at fixed temperature $T = 310$ K is shown in the inset in Fig. 2(a). We assume that the granular film is placed above the P(VDF/TrFE) relaxor FE. For the dependence of dielectric permittivity of P(VDF/TrFE) on the external field we use the data of Ref. 31 with some smooth function to describe the data. The granular film has the following parameters: the average grain size $a = 3$ nm, the inter-grain distance $r_g = 7$ nm, the dielectric permittivity of insulating matrix $\epsilon_m = 1$, the effective dielectric permittivity of the half-space above the substrate $\epsilon = 1.3$, the distance between the film and the substrate $h = 4$ nm.

The hysteresis in the charging energy leads to the hysteresis in the resistance of granular film, Fig. 2(b). The

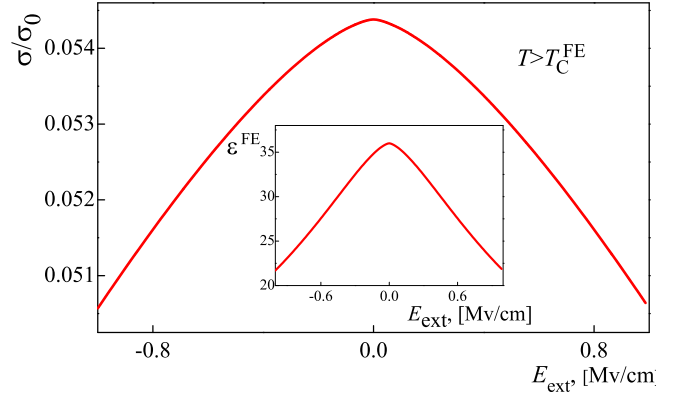


FIG. 4. (Color online) Normalized conductivity of granular film vs external electric field E_{ext} for temperatures $T = 390\text{ K} > T_C^{\text{FE}}$. Insert: Dielectric permittivity of the FE substrate vs external electric field.

resistance difference between the hysteresis branches is important for memory applications. The maximum difference occurs in the vicinity of the switching field E_s . We introduce the dielectric permittivity of the FE substrate for these two states as ϵ_1^{FE} and ϵ_2^{FE} . Substituting Eq. (1) into Eq. (5) we find

$$\Delta_r = 2 \frac{\sigma(\epsilon_1^{\text{FE}}) - \sigma(\epsilon_2^{\text{FE}})}{\sigma(\epsilon_1^{\text{FE}}) + \sigma(\epsilon_2^{\text{FE}})} = \tanh \left(\frac{2e^2}{hT} \frac{\epsilon_1^{\text{FE}} - \epsilon_2^{\text{FE}}}{(\epsilon_1^{\text{FE}} + \epsilon)(\epsilon_2^{\text{FE}} + \epsilon)} \right). \quad (6)$$

The conductivity difference in Eq. (6) increases with decreasing the film thickness. The minimum thickness for considered system is the grain size, $h = a$. The conductivity difference depends on the external electric field E_{ext} and can be rather big, Fig. 3.

The conductivities ratio for different FE dielectric permittivity can be estimated as $\sigma(\epsilon_2^{\text{FE}})/\sigma(\epsilon_1^{\text{FE}}) \approx \exp(-(e^2/Th)((\epsilon_2^{\text{FE}} - \epsilon_1^{\text{FE}})/(\epsilon_2^{\text{FE}}\epsilon_1^{\text{FE}})))$. At room temperature the factor e^2/Th is $\sim 5 - 10$. The second factor in the exponent is less than 1 and can reach 0.3. Therefore the maximum ratio $\sigma(\epsilon_2^{\text{FE}})/\sigma(\epsilon_1^{\text{FE}})$ is about 10. In this paper this ratio is less due to the small difference between ϵ_2^{FE} and ϵ_1^{FE} .

In the low temperature limit, $T < T_{\text{cr}}$, where the VRH is the main transport mechanism the conductivity difference should be calculated using Eq. (2). In this case Δ_r can not be written in a simple form. Generally, the conductivity difference is given by the expression

$$\Delta_r = \tanh \left(\frac{\sqrt{T_0(\epsilon_2^{\text{FE}})} - \sqrt{T_0(\epsilon_1^{\text{FE}})}}{2\sqrt{T}} \right). \quad (7)$$

E. Conductivity above the Curie point

For temperatures $T > T_C^{\text{FE}}$ the spontaneous polarization in the FE layer is absent. In this limit the dielec-

tric permittivity is unambiguous function of the external electric field E_{ext} with no hysteresis. It monotonically decreases with electric field. The conductivity σ has similar behavior, Fig. 4. Plots in Fig. 4 correspond to the granular film placed above the P(VDF/TrFE) relaxor FE substrate with the same parameters as discussed before.

F. Conductivity temperature dependence

The temperature dependence of conductivity of granular film placed above the FE substrate is shown in Fig. 5. Different curves correspond to different external electric fields E_{ext} . Three upper curves correspond to granular film placed above the substrate at distance $h = 4$ nm and with average grain size 4 nm. The lower solid line stands for conductivity of granular film without FE substrate. We use the data of Ref. 31 for dielectric permittivity of the FE substrate. The temperature dependence of dielectric permittivity is essentially different from the Weiss law since P(VDF/TrFE) is the relaxor ferroelectric.^{32–34}

The dielectric permittivity ϵ^{FE} of the FE substrate strongly depends on temperature in the vicinity of the FE-paraelectric phase transition, insert in Fig. 5. It has a maximum at temperature $T = T_C^{\text{FE}}$ leading to the maximum in conductivity. The maximum appears due to the suppression of Coulomb blockade. This is in contrast to the usual situation where conductivity decreases in the vicinity of phase transition due to the increase of current carriers scattering by the order parameter fluctuations.

The change of conductivity on temperature has the form

$$\frac{\partial \sigma}{\partial T} = \frac{\sigma E_c^0}{T} \left\{ \frac{1}{\epsilon T} \left(1 + \frac{a(\epsilon - \epsilon^{\text{FE}})}{h(\epsilon + \epsilon^{\text{FE}})} \right) + \frac{2a(\epsilon^{\text{FE}})'_T}{h(\epsilon + \epsilon^{\text{FE}})^2} \right\}. \quad (8)$$

For large dielectric permittivity of the FE substrate, $\epsilon^{\text{FE}} \gg \epsilon$, we find

$$\frac{\partial \sigma}{\partial T} = \frac{\sigma E_c^0}{T} \left\{ \frac{1}{\epsilon T} \left(1 - \frac{a}{h} \right) + \frac{2a(\epsilon^{\text{FE}})'_T}{h(\epsilon^{\text{FE}})^2} \right\}. \quad (9)$$

Using phenomenological theory of phase transitions we write the dielectric permittivity of conventional ferroelectrics as follows,³⁵

$$\epsilon^{\text{FE}} \approx \begin{cases} \frac{1}{\alpha(T - T_C^{\text{FE}})}, & T > T_C^{\text{FE}}, \\ \frac{1}{2\alpha(T_C^{\text{FE}} - T)}, & T < T_C^{\text{FE}}. \end{cases} \quad (10)$$

Here α is the phenomenological constant.³⁵ Substituting Eq. (10) into Eq. (8) we obtain

$$\frac{\partial \sigma}{\partial T} = \frac{\sigma E_c^0}{T} \left\{ \frac{1}{\epsilon T} \left(1 - \frac{a}{h} \right) - \frac{2a\alpha/h}{(T - (T_C^{\text{FE}})^2)\alpha^2\epsilon + 1}, T > T_C^{\text{FE}}, \right. \\ \left. \frac{1}{\epsilon T} \left(1 - \frac{a}{h} \right) + \frac{4a\alpha/h}{(T - (T_C^{\text{FE}})^2)4\alpha^2\epsilon + 1}, T < T_C^{\text{FE}}. \right\} \quad (11)$$

The temperature derivative of conductivity is discontinuous at the transition point leading to the kink in conductivity. In reality the kink is smeared because

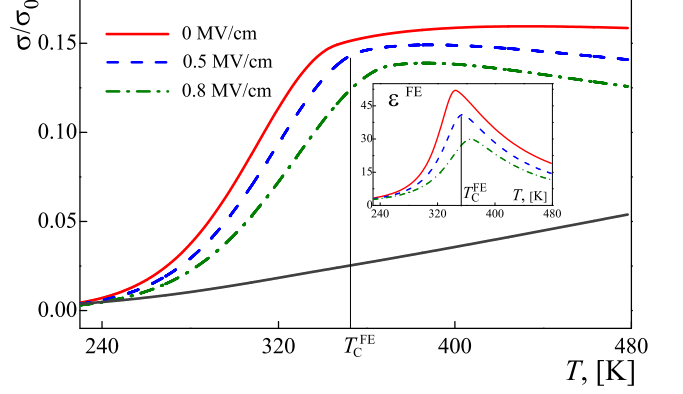


FIG. 5. (Color online) Normalized conductivity of granular film placed above the P(VDF/TrFE) substrate vs temperature for different electric fields. Insert: dielectric permittivity of the FE substrate vs temperature. The black solid line stands for conductivity of granular film without FE substrate.

the phenomenological Landau-Ginzburg-Devonshire theory is valid only beyond the Ginzburg region.³⁶

The influence of the FE substrate is more pronounced for temperatures $T < T_C^{\text{FE}}$, below the FE transition, if the following condition is satisfied

$$\frac{2a}{h} \epsilon \alpha T > 1. \quad (12)$$

Equation (12) has transparent physical meaning: the dielectric permittivity of FE should be smaller than the dielectric permittivity of granular film ϵ at distance $1/(\alpha T)$ away from the phase transition.

In the low temperature limit, $T < T_{\text{cr}}$, the change of conductivity on temperature is defined by the expression

$$\frac{\partial \sigma}{\partial T} = \frac{\sigma}{\sqrt{T T_0}} \left(\frac{2e^2}{\epsilon a} \left(\frac{2E_c^0 a \epsilon (\epsilon^{\text{FE}})'_T}{E_c h (\epsilon + \epsilon^{\text{FE}})^2} + \frac{1}{T} \right) + \frac{T_0}{T} \right). \quad (13)$$

Recently the conductivity of Pt based nanogranular metal placed above the TTF-CA organic ferroelectric was studied experimentally.³⁷ The data show a peculiar behavior of granular film conductivity on temperature in the vicinity of the FE Curie point. The conductivity has a maximum at temperature $T = T_C^{\text{FE}}$. These results are in a good agreement with our predictions: the conductivity peak exists due to the decreasing of charging energy in granular film in the vicinity of the Curie temperature, T_C^{FE} .

III. DISCUSSION

A. Memory cell

Composite system of granular and FE films can be used as a memory cell with data storage in the direction of polarization of the FE film.

Writing of data (switching between different states) is achieved by the external electric field, E_{ext} or the gate voltage, Fig. 1. The field E_{ext} should be larger than the FE switching field E_s . The sign of E_{ext} depends on the FE state.

Reading of data (polarization direction) is achieved by a small reading bias voltage and a positive gate voltage. The gate voltage should be smaller than the switching voltage to prevent the polarization switching. In Sec. IIID we discuss the characteristic time scales.

B. Electric field sensors

The dependence of conductivity σ of granular film on the external electric field can be used in the electric field measuring devices with sensitivity being defined as follows $\chi = \sigma^{-1} \partial \sigma / \partial E_{\text{ext}} = -2e^2 (\epsilon^{\text{FE}})'_{E_{\text{ext}}} / T h(\epsilon + \epsilon^{\text{FE}})^2$. Below the Curie temperature the field derivative (sensitivity), $\partial \sigma / \partial E_{\text{ext}}$, is finite at zero external field E_{ext} . The sensitivity is defined by the slope of the dependence of dielectric permittivity on the electric field. Therefore the large sensitivity can be achieved for the FE substrate with strong field dependent dielectric permittivity.

C. Temperature sensors

The fact that the FE substrate can enhance the temperature dependence of conductivity of granular film below the FE curie point can be used in temperature measurements. The temperature sensitivity of such a system can be tuned by an external electric field.

D. Timescales

Here we discuss two characteristic timescales in this problem: 1) the electron hopping time between grains, $\tau_e = R_g C_g$ with R_g and C_g being the intergrain resistance and the grain capacitance, respectively, and 2) the polarization switching time, τ_P .

Our consideration is valid for $\tau_P \ll \tau_e$ meaning that the polarization effectively screens the excess electron electric field and the image charge has enough time to form while the excess electron is present at a certain grain. Physically this limit corresponds to the hopping of coupled pair of electron and the image charge instead of a single electron hopping which correspond to the opposite limit, $\tau_P \gg \tau_e$. In this case it is necessary to average the interaction of the FE film with the electric field created by electrons over the large timescale. This leads to the suppression of screening effect and disappearance of coupling between the FE and the granular film. For a single electron transistor with the FE this effect was discussed in Ref. 38.

For $\tau_P \ll \tau_e$ the highest possible performance frequency for memory applications is $1/\tau_e$.

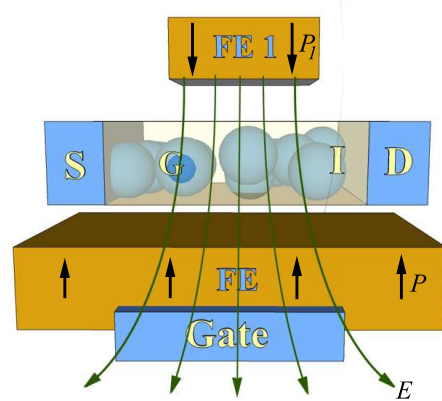


FIG. 6. (Color online) Granular film between two ferroelectrics. Bottom FE stores the data (polarization direction). Upper FE particle with fixed polarization P_1 creates the bias electric field (E) for data reading.

To investigate the system behavior for arbitrary time τ_e one needs to take into account time dispersion of the FE response and solve time dependent equations for the FE substrate and grains.

Characteristic time τ_e varies in a rather large range from dozens of nano- to picoseconds. This time is controlled by the system geometry and materials. The FE switching time τ_P depends on the material and can be in the range of 10^{-6} s³⁹ to few nanoseconds.⁴⁰ Therefore both limits are relevant for experiment.

E. Reading without gate voltage

For data reading one can use the stray field of the FE particle placed above the granular film instead of external electric field produced by the gate electrode, Fig. 6. A small FE particle with fixed polarization perpendicular to the film surface creates a stray electric field acting on the bottom FE layer as an external field, E_{ext} .

F. Ultimate size of granular FE memory

Reducing the size of granular film one can reach the ultimate size of memory element - a single grain. In this limit the memory cell is the single electron transistor consisting of a metallic grain located between two leads. The transport properties of this system were discussed in Ref. 38.

IV. CONCLUSION

We studied electron transport properties of granular film placed above the FE substrate. We showed that the conductivity of granular film strongly depends on the FE state due to screening effects which changes the

Coulomb energy in the granular film. We showed that the FE/granular film system has a large electro-resistance effect. The conductivity of granular film depends on the direction of the FE polarization. This effect can be utilized in memory and electric field sensors applications. We showed that the conductivity of the FE/granular film system strongly depends on temperature in the vicinity of the FE-paraelectric phase transition. In particular, the conductivity has a peak at the Curie point in contrast to the usual situation where conductivity decreases in the vicinity of phase transition. This effect can be used in temperature sensing devices.

ACKNOWLEDGMENTS

We thank Michael Huth for providing us with his manuscript prior publication. N. C. was supported by RFBR No. 13-02-00579, the Grant of President of Russian Federation for support of Leading Scientific Schools No. 6170.2012.2, RAS presidium and Russian Federal Government programs. I. B. was supported by NSF under Cooperative Agreement Award EEC-1160504, NSF Award DMR-1158666, and NSF PREM Award.

Appendix A: Grain charges in equilibrium

Here we discuss the relation between the grain charges q^g and the applied gate voltage V_g using the following model: All grains have the same size and the same distance above the FE substrate. We consider the granular film as an effective medium with dielectric permittivity ϵ_{eff} assuming that $\epsilon_{\text{eff}} \approx \epsilon_1$.

We consider a certain grain G and find the electric field along the shortest line connecting the grain center and the gate electrode. The field along this line is created by the grain G , all other grains, charges on the FE surface and the gate electrode. We model all grains except the grain G as a homogeneously charged plane with a hole of radius r_g around the grain G . The electric field created by the grain G in vacuum is $E_g = q^g/z^2$, where z is the coordinate perpendicular to the FE surface. The origin of the z -axis is in the center of grain G . The electric field created by the charged plane with a hole is given by the superposition of homogeneous plane and the oppositely charged disk (in vacuum this field is $E_{\text{disk}} = 2\pi\sigma^g(1 - z/((z^2 + r_g^2)^{1/2}))$), where σ^g is the average surface density of the charges at the grains layer. In the vicinity of the grain G the field is strongly inhomogeneous due to inhomogeneous charge distribution. Away from the grain, $z \gg r_g$, the field turns into the uniform field of charged plane.

The FE substrate is characterized 1) by the polarization P which is perpendicular to the FE surface and depends on the average electric field inside the FE and 2) by the anisotropic dielectric permittivity tensor $\hat{\epsilon}^{\text{FE}}$. We assume that one of the main axis of the FE is co-directed

with the z -axis. Since the boundary conditions at the FE surface includes only the perpendicular component of electric induction only the z -component of $\hat{\epsilon}^{\text{FE}}$ is important. We denote this component as ϵ^{FE} . It depends on the electric field applied to the FE. The uniform polarization of the FE film P leads to the appearance of surface electric charges on the FE surface $\sigma^P = \pm P$, where the sign "±" describes the opposite FE surfaces.

Since the dielectric permittivity of the FE is much larger than the permittivity of the insulating matrix above the FE substrate the field produced by the grain G and by the opposite charged disk create the image charges inside the FE film. The electric field inside the insulating layer, between the grains and the FE substrate, is given by the sum of electric field created by the grains and their images. The image charges are $q^g(\epsilon_1 - \epsilon^{\text{FE}})/(\epsilon_1 + \epsilon^{\text{FE}})$. To calculate the electric field inside the FE we use the effective charge $q^g 2\epsilon_1/(\epsilon_1 + \epsilon^{\text{FE}})$ for the grain G charge and the disk charge. We neglect the images appearing due to the gate since the distance between grains and the gate is large.

We estimate the potential difference between the grain G and the electrode in the leading approximation as follows $\Delta\phi \approx 4\pi\sigma^g(h-a)/\epsilon_1 + 4\pi(\sigma^g + P)L/\epsilon^{\text{FE}} + 2\pi\sigma^g(h-a)\epsilon^{\text{FE}}/(ah\epsilon_1(\epsilon_1 + \epsilon^{\text{FE}}))$. We use the following set of parameters: $h - a \approx 1$ nm, $\epsilon_1 \approx 5$, $\epsilon^{\text{FE}} \approx 30$ and the FE thickness is ~ 300 nm to reduce the depolarizing electric field inside the FE by the order of magnitude. For these parameters the screening charges at zero gate voltage are $\sim 0.9 P r_g^2$.

The screening of the FE polarization by the grains is suppressed for intergrain distances larger than the grain size. In addition, the insulating layer between the granular layer and the FE reduces the screening. The screening is small for FE with high dielectric permittivity, $\epsilon^{\text{FE}} > 1000$.

At finite gate voltage the screening charge is given by the expression

$$q^g = \frac{V_g - 4\pi LP/\epsilon^{\text{FE}}}{\frac{4\pi(h-a)}{\epsilon_1} + \frac{4\pi L}{\epsilon^{\text{FE}}} + \frac{2\pi(h-a)\epsilon^{\text{FE}}}{(ah\epsilon_1(\epsilon_1 + \epsilon^{\text{FE}}))}}. \quad (\text{A1})$$

Appendix B: Coulomb energy

1. Simplified model

Here we discuss the derivation of the charging energy in Eq. (1),²⁷. We consider a simple model qualitatively describing the influence of the FE substrate on the Coulomb energy in granular film. We consider a metallic sphere with radius a and charge e placed above the FE at distance h , $a < h$, Fig. 7. The external electric field E_{ext} is applied in the z direction perpendicular to the FE surface. In the previous section we discussed the ground state assuming that all grains have the same charge. The ground state is defined by the mutual capacitance of the

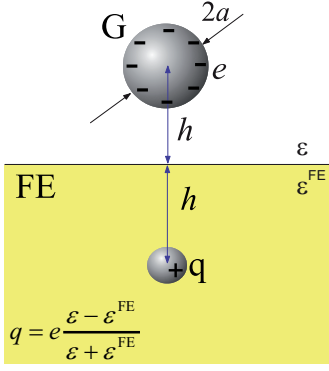


FIG. 7. (Color online) Single metallic grain with size $2a$ and charge e at distance h above the FE substrate. ϵ is the dielectric permittivity of the medium above the FE substrate. ϵ^{FE} is the dielectric permittivity of the FE substrate. q is the image charge appearing in the FE substrate. Interaction of metallic grain with the image charge modifies the grain charging energy E_c .

whole granular film and the gate electrode. Here we estimate the electrostatic energy of a single excess electron placed at a certain grain. In this case the capacitance of a single grain with respect to the whole system (all other grains and the FE substrate) is important.

The FE substrate is characterized by the polarization vector \mathbf{P} and the dielectric permittivity tensor $\hat{\epsilon}^{\text{FE}}$ with ϵ^{FE} being its z-component. This description is valid for field created by the grains being smaller than the switching field of the FE. Both polarization and the permittivity depend on the external electric field E_{ext} .

Above the FE substrate there is a medium with an effective dielectric permittivity ϵ accounting for all other grains and the insulating matrix. We assume that ϵ does not depend on the external electric field. The charged sphere induces the image charge inside the FE substrate. The magnitude of the image charge is $e(\epsilon - \epsilon^{\text{FE}})/(\epsilon + \epsilon^{\text{FE}})$. Since the dielectric permittivity of the FE is larger than that of the insulator, the image charge has the opposite sign with respect to the charge of the grain. The interaction of the charged sphere with the image charge reduces the electrostatic energy. This effect can be thought of as the effective screening of the electric field created by electrons on the grains by the FE substrate leading to the reduction of the charging energy. As a result we obtain the renormalized Coulomb energy, E_c in Eq. (1).

2. Coulomb energy in multilayer system

In general, the granular system consists of several layers with different dielectric permittivities. In the simplified model we used the effective dielectric permittivity ϵ to describe the layers above the FE substrate. However, this approximation is valid for the dielectric permittivity of the granular film and the dielectric permittivity of the insulator below and above the film being close in

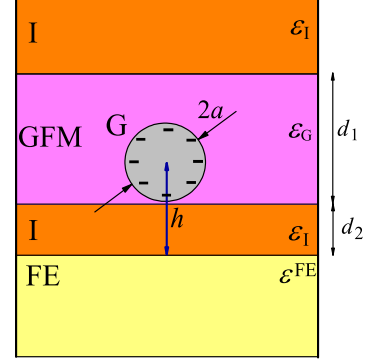


FIG. 8. (Color online) Multilayer system consisting of FE substrate (FE) with dielectric constant ϵ^{FE} , insulating layers (I) with dielectric constants ϵ_I and granular film (GF). Metallic grain (G) of size $2a$ is located above the FE substrate at distance h . Space around the grain in granular film is considered as an effective medium with dielectric constant ϵ_G . Granular film and the middle insulating layer have thickness d_1 and d_2 , respectively.

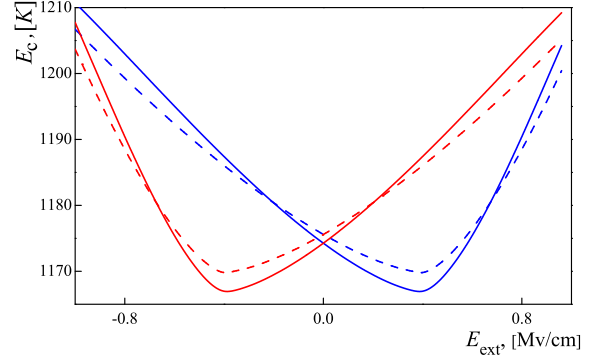


FIG. 9. (Color online) Single grain charging energy placed in layered system shown in Fig. 8. $d_1 = 1$ nm, $d_2 = 7$ nm, $\epsilon_G \approx 1.3$, $\epsilon_I = 1$. The FE is the P(VDF/TrFE) relaxor. Dashed lines correspond to the charging energy calculated using Eq. (1). Solid lines correspond to the numerical method for layered structure.

magnitude.

Below we calculate the charging energy for a grain located in a layered system. To calculate the charging energy we use the point charges collocation method.^{41,42} The charging energy of metallic grain placed in a system consisting of several insulating layers (see Fig. 8) can be estimated as $E_c = e^2/(2C)$ with C being the grain capacitance.

To find the capacitance C we consider the sphere as the ensemble of point charges q_i placed in the positions \mathbf{r}_i . We find charges q_i self-consistently assuming that all the points \mathbf{r}_i have the same potential $\phi_i = \phi$ and the total charge of the sphere is $Q = \sum q_i$. The potential at

points \mathbf{r}_i can be found as

$$\phi_i = \phi = \sum_j q_j G_{ij}, \quad (\text{B1})$$

where G_{ij} is the electric potential created at point \mathbf{r}_i by the unit charge located at point \mathbf{r}_j . The Green functions G_{ij} for layered system can be found using the two dimensional Fourier transformation. The capacitance $C = Q/\phi$ can be calculated after solving Eqs. B1.

We calculate the charging energy E_c as a function of

electric field for the following system: the granular film is placed above the P(VDF/TrFE). The grain radius is $a = 3$ nm, the height is $h = 4$ nm ($d_2 = 1$ nm), the inter-grain distance is $r_g = 7$ nm, the thickness of the granular film is $d_1 = 7$ nm and the effective dielectric permittivity is $\epsilon_G \approx 1.3$. The solid lines in Fig. 9 shows the charging energy vs. field E_{ext} calculated using numerical method. The dashed lines stand for curves obtained using Eq. (1). The numerical calculations with more complicated model produce almost the same result as the simplified model. However, the difference increases with increasing the difference $\epsilon_I - \epsilon_G$.

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- ¹ A. V. Bune, V. M. Fridkin, S. Ducharme, L. M. Blinov, S. P. Palto, A. V. Sorokin, S. G. Yudin, and A. Zlatkin, *Nature* **391**, 874 (1998).
 - ² I. I. Naumov, L. Bellaiche, and H. Fu, *Nature* **432**, 737 (2004).
 - ³ V. M. Fridkin, R. V. Gaynutdinov, and S. Ducharme, *Sov. Phys. Usp.* **53**, 199 (2010).
 - ⁴ J. F. Scott, *Science* **315**, 5814 (2007).
 - ⁵ Z. Hu, M. Tian, B. Nysten, and A. M. Jonas, *Nature Mat.* **8**, 62 (2009).
 - ⁶ V. M. Fridkin, *Sov. Phys. Usp.* **49**, 193 (2006).
 - ⁷ W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature* **442**, 759 (2006).
 - ⁸ V. Garcia, M. Bibes, L. Bocher, S. Valencia, F. Kronast, A. Crassous, X. Moya, S. Enouz-Vedrenne, A. Gloter, D. Imhoff, C. Deranlot, N. D. Mathur, S. Fusil, K. Bouzehouane, and A. Barthelémy, *Science* **327**, 1106 (2010).
 - ⁹ E. Y. Tsymbal and H. Kohlstedt, *Science* **313**, 181 (2006).
 - ¹⁰ D. Pantel and M. Alexe, *Phys. Rev. B* **82**, 134105 (2010).
 - ¹¹ M. Y. Zhuravlev, R. F. Sabirianov, S. S. Jaswal, and E. Y. Tsymbal, *Phys. Rev. Lett.* **94**, 246802 (2005).
 - ¹² P. W. M. Blom, R. M. Wolf, J. F. M. Cillessen, and M. P. C. M. Krijn, *Phys. Rev. Lett.* **73**, 2107 (1994).
 - ¹³ X. Liu, Y. Wang, J. D. Burton, and E. Y. Tsymbal, *Phys. Rev. B* **88**, 165139 (2013).
 - ¹⁴ T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, and S.-W. Cheong, *Science* **324**, 63 (2009).
 - ¹⁵ P. Maksymovych, S. Jesse, P. Yu, R. R. and Arthur P. Bad-dorf, and S. V. Kalinin, *Science* **324**, 1421 (2009).
 - ¹⁶ P. M. Heyman and G. H. Hlilmeier, *Proc. IEEE* **54**, 842 (1966).
 - ¹⁷ S. L. Miller and P. J. McWhorter, *J. Appl. Phys.* **72**, 5999 (1992).
 - ¹⁸ S. Mathews, R. Ramesh, T. Venkatesan, and J. Benedetto, *Science* **276**, 238 (1997).
 - ¹⁹ O. G. Udalov, N. M. Chtchelkatchev, A. Glatz, and I. S. Beloborodov, *Phys. Rev. B* **89**, 054203 (2014).
 - ²⁰ K. V. Reich, T. Chen, and B. I. Shklovskii, (2014), arXiv:1403.4154 [cond-mat].
 - ²¹ E. J. Mele, *Am. Jour. Phys.* **69**, 557 (2001).
 - ²² S. H. Lim, A. C. Rastogi, and S. B. Desu, *J. Appl. Phys.* **96**, 5673 (2004).
 - ²³ C. L. Sun, S. Y. Chen, C. C. Liao, and A. Chin, *J. Appl. Phys.* **85**, 4726 (2004).
 - ²⁴ P. Sheng, B. Abeles, and Y. Arie, *Phys. Rev. Lett.* **31**, 44 (1973).
 - ²⁵ I. S. Beloborodov, A. V. Lopatin, V. M. Vinokur, and K. B. Efetov, *Rev. Mod. Phys.* **79**, 469 (2007).
 - ²⁶ O. G. Udalov, N. M. Chtchelkatchev, and I. S. Beloborodov, *Phys. Rev. B* **89**, 174203 (2014).
 - ²⁷ O. G. Udalov, N. M. Chtchelkatchev, and I. S. Beloborodov, (2014), arXiv:1402.3565 [cond-mat].
 - ²⁸ A. L. Efros and B. I. Shklovskii, *J. Phys. C: Solid State Phys.* **8**, L49 (1975).
 - ²⁹ T. Chen, B. Skinner, and B. I. Shklovskii, *Phys. Rev. Lett.* **109**, 126805 (2012).
 - ³⁰ I. S. Beloborodov, A. V. Lopatin, and V. M. Vinokur, *Phys. Rev. B* **72**, 125121 (2005).
 - ³¹ H. Ryu, P. Murugavel, J. H. Lee, S. C. Chae, T. W. Noh, Y. S. Oh, H. J. Kim, K. H. Kim, J. H. Jang, M. Kim, C. Bae, and J.-G. Park, *Appl. Phys. Lett.* **89**, 102907 (2006).
 - ³² G. A. Smolensky, *J. Phys. Soc. Jpn. Suppl.* **28**, 26 (1970).
 - ³³ Z.-Y. Cheng, R. S. Katiyar, X. Yao, and A. Guo, *Phys. Rev. B* **55**, 8165 (1997).
 - ³⁴ Z.-Y. Cheng, R. S. Katiyar, X. Yao, and A. S. Bhalla, *Phys. Rev. B* **57**, 8166 (1998).
 - ³⁵ B. A. Strukov and A. P. Levanyuk, *Ferroelectric Phenomena in Crystals* (Springer, Geidelberg, 1998, 1998).
 - ³⁶ L. D. Landau and I. M. Lifshitz, *Statistical Physics, Part 1. Vol. 5 (3rd ed.)*. (ButterworthHeinemann., 1980).
 - ³⁷ M. Huth, A. Rippert, R. Sachser, and L. Keller, (2014), arXiv:1404.7669 [cond-mat].
 - ³⁸ S. A. Fedorov, A. E. Korolkov, N. M. Chtchelkatchev, O. G. Udalov, and I. S. Beloborodov, *Phys. Rev. B* **89**, 155410 (2014).
 - ³⁹ H. Hu and S. B. Krupanidhi, *J. Appl. Phys.* **74**, 3373 (1993).
 - ⁴⁰ P. K. Larsen, G. L. M. Kampschoer, M. J. E. Ulenaers, G. A. C. M. Spierings, and R. Cuppens, *Appl. Phys. Lett.* **59**, 611 (1991).
 - ⁴¹ M. Huth, F. Kolb, and H. Plank, (2014), arXiv:1404.3541 [cond-mat].
 - ⁴² C. Wasthuber, *Computational Single-Electronics* (Springer, Wien/New York, 2001).